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Outgassing Rates in Polymeric Foams

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ABSTRACT

Diffusion rates for carbon dioxide were determined on closed-cell polyurethane foams of varying densities by monitoring, for two to three weeks, the loss of weight from specimens suspended in a vacuum of 10^- mm Hg. The experimental data were used to calculate diffusion coefficients for these materials, which were found to be of the order of 10^{-6} to 10^{-5} cm^2/sec between 22 and 81 °C.

The solution of the diffusion equation for an idealized model for a foam yielded the following expression for the diffusion coefficient:

$$D = P_e' \left(\frac{RT}{M}\right)\left(\frac{\rho_0}{\rho}\right)\left[\frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3}\right]$$

which relates the diffusion coefficient D to the foam density ρ and to the permeation constant P_e and the density ρ_0 of the bulk polymer; R is the gas constant, T the temperature, and M the molecular weight of the gas.

Using this equation and experimentally obtained values of D, a P_e of 5.1×10^{-3} (cc STP) mm/sec/cm^2/cm Hg was calculated for the polyurethane material comprising the foam, which agrees within a factor of 2 for reported P_e constants for polyurethane.

I. INTRODUCTION

Currently, there is considerable interest in the possibility of using polymeric foams as lightweight encapsulants for electronic components on spacecraft. Very little is known, however, on the electrical breakdown behavior in foams, where an important parameter is the pressure of the blowing gas within the foam cells; in particular, in the ionization region for the gas. Therefore, a study was undertaken of the diffusion of the blowing gas from foams when placed in high vacuum. The fundamental aspects of this process are of importance to the general problem of transport properties of inhomogeneous synthetic or natural polymeric systems.

The purpose of this Report is to present: (1) a relationship that was developed to relate the diffusion constant for a foam to its density and the permeation constant of the bulk polymer, (2) a description of the experimental techniques used for this study, and (3) experimental results obtained on closed-cell polyurethane foams.

II. DIFFUSION EQUATIONS

Diffusion equations for polymeric foams were developed using as a simple, but physically reasonable model, a three-dimensional array of cubical cells having walls of uniform thickness and permeable to gases. Here, only one-dimensional diffusion is considered, although extension to the three-dimensional case is straightforward.

The general relation for the flux J at which a gas permeates through a membrane is

$$J = \frac{dw}{dt} = \frac{P_e A}{L} \Delta P \tag{1}$$

where

w = weight of gas

P_e = permeation constant

A = area

L = thickness of membrane

ΔP = pressure difference across the membrane

t = time

The net flux for the nth layer of cells is given by

$$\frac{dw_n}{dt} = J_{n-1} - J_{n-1} \tag{2}$$

which, upon substituting for J, yields

$$\frac{L}{P_e A} \frac{dw_n}{dt} = P_{n+1} - 2P_n + P_{n-1} \tag{3}$$

From the perfect gas law,

$$w_n = P_n \frac{VM}{RT} \tag{4}$$

which can be substituted into Eq. (3) to yield the following differential equation:

$$\frac{LVM}{P_e ART} \frac{dp_n}{dt} = P_{n-1} - 2P_n + P_{n+1} \tag{5}$$

for the pressure P_n in the nth layer of cells.

Thus for a system of N layers, we have a set of N linear homogeneous equations. For the boundary condition that the external pressure is always zero, along with the initial condition that for zero time the pressure P_0

in all layers is uniform, the following relationship is obtained:

$$\frac{P_n(t)}{P_0} = \sum_{k=1}^{N} \alpha_k \left[\sin \frac{\pi n (2k-1)}{2N+1} \right]$$
$$\times \exp \left\{ - \left(\frac{P_e ART}{LVM} \right) \left[2 - 2 \cos \frac{\pi (2k-1)}{2N+1} \right] t \right\} \tag{6}$$

For the limiting case of $N \to \infty$, the coefficients α_k's can be readily evaluated, and the solution becomes

$$\frac{P_n(t)}{P_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left[\frac{\pi (2k-1) n}{2N} \right]$$
$$\times \exp \left\{ - \left(\frac{P_e ART}{LVM} \right) \left[\frac{\pi (2k-1)}{2N} \right]^2 t \right\} \tag{7}$$

If $N > 20$, values of α_k's for the limiting case of $N \to \infty$ can be used without introducing a significant error. Inasmuch as for a 1-in.-thick foam, N is of the order of a few hundred, Eq. (7) is applicable for all cases of interest. Now, if formally we consider the gas as a diffusion process in a medium characterized by a diffusion constant D, the following well-known equation is appropriate (Ref. 1):

$$\frac{P_x}{P_0} = \frac{C_x}{C_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left[\frac{\pi x (2k-1)}{2a} \right]$$
$$\times \exp \left\{ - \left[\frac{(2k-1) \pi}{2a} \right]^2 Dt \right\} \tag{8}$$

where

C_x = concentration of gas

C_0 = initial concentration

a = thickness of solid

x = distance in from exposed surface

D = diffusion constant

This equation is identical to Eq. (7) only at the limit $N \to \infty$. But, again it will be a close enough approximation for large N. Noting that since $n/N = x/a$, the coefficients in both equations are identical and hence the arguments of the exponential for Eq. (7) and (8) must be equal; thus

$$\frac{D}{a^2} = \frac{P_e ART}{LVMN^2} \tag{9}$$

As V/A is the length of the side of a cell d, we substitute and rearrange Eq. (9) to get

$$D = P_e \left(\frac{RT}{M}\right) \frac{a^2}{(NL)(Nd)} \qquad (10)$$

As a is the thickness of the foam and NL and Nd are the thickness of the membranes and the cells respectively, it follows that $a = NL + Nd$. The ratio $a^2/\{(NL) \times (Nd)\}$ can be readily expressed in terms of the densities of the foam ρ and the bulk polymer ρ_0. For a cube of unit dimensions, i.e., $c = 1$, which contains N^3 cells, the total volume of cells is $(Nd)^3$. This volume represents the volume fraction of voids and is therefore equal to $(1 - \rho/\rho_0)$. Thus (Nd) is equal to $(1 - \rho/\rho_0)^{1/3}$ and since $(Nd) + (NL) = 1$, (NL) is equal to $1 - (1 - \rho/\rho_0)^{1/3}$. Substituting for (NL) and (Nd) in Eq. (10) and factoring out ρ_0/ρ, the following expression is obtained:

$$D = P_e \left(\frac{RT}{M}\right)\left(\frac{\rho_0}{\rho}\right)\left[\frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3}\right] \qquad (11)$$

where

ρ = density of foam

ρ_0 = density of membrane material

Equation (11) relates the diffusion constant of a polymer foam to the permeation constant and foam density. The expression

$$\left[\frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3}\right]$$

varies slowly between 3 and 3.05 as ρ/ρ_0 varies between 0 and 0.5. Since most polymer foams are of low density, the variation in this term can be neglected. Thus for a given family of foams, Eq. (11) predicts that the diffusion constant is inversely proportional to the foam density and can be simply represented as

$$D = K/\rho \qquad (12)$$

The experimental data are obtained by measuring the weight loss of gas Q, from polymer foams in vacuum. The value of D is then calculated by use of the integrated form of Eq. (8) (Ref. 1):

$$Q = Q_\infty - \frac{8Q_\infty}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2} \exp\left\{-\left[\frac{(2k-1)\pi}{2a}\right]^2 Dt\right\} \qquad (13)$$

where Q_∞ is the initial weight of gas in the foam. For sufficiently long enough times, all the exponential terms except the first ($k = 1$) can be neglected. Thus a plot of $\ln(Q_\infty - Q)$ vs time will eventually become linear with a slope of $[\pi/2a]^2 D$.

III. EXPERIMENTAL

To obtain weight-loss data, foams of 3-in. diameter and 1-in. deep were bonded into aluminum containers, leaving the top surface exposed. The bonding agent was Eccobond 55*, a room-temperature curing epoxy.

Weight-loss data at room temperature, $22 \pm 1°C$, were obtained with an Ainsworth vacuum balance unit. The balance and details of sample suspension are shown in Fig. 1 and 2.

For elevated temperatures, weight loss was measured with a Cahn RH Electrobalance, which was situated inside a vacuum unit manufactured by the Consolidated Vacuum Corporation. The sample was heated by means of a variac-controlled 250-w bulb. A temperature differential of less than one degree was maintained across the sample by means of a reflecting aluminum shroud (Fig. 3 and 4).

The following polymer foams were investigated:

1. Eccosil 5000*, a syntactic silicone foam of nominal sp. gr. 0.48, prepared by mixing together hollow silicone spheres and a silicone resin.

2. Eccofoam SH*, a nominal 8-lb/ft^3 polyurethane foam filled with CO_2 gas. This material is purchased already blown in 1-in.-thick sheet stock. Actual measured density of the sample was 7.6 lb/ft^3.

3. Stycast 1090*, a syntactic epoxy foam prepared by mixing together hollow glass spheres and an epoxy

resin. System cures hard with a nominal sp. gr. of 0.78.

4. Eccofoam FPH/12/2H*, a nominal 2-lb/ft^3 polyurethane foam filled with CO_2 gas. Material prepared prior to test by mixing a resin-catalyst system and allowing the combination to foam and cure. Density of sample was 2.1 lb/ft^3.

5. Eccofoam FPH/12/6H*, a nominal 6-lb/ft^3 polyurethane foam filled with CO_2 gas. Material prepared prior to test by mixing a resin-catalyst system together and pouring into a mold 2 in. deep and 3 in. in diameter. Using an appropriate weight schedule, the foaming reaction would result in about half of the cured material extending above the top of the mold. Samples prepared from the top and bottom halves were found to be 4.5 and 6.4 lb/ft^3, respectively.

The family of rigid, closed-cell polyurethane foams known as Eccofoams FPH are asserted by the manufacturer to be capable of withstanding indefinite exposure to a temperature of 300°C, and even to higher temperatures for short periods of time. These materials are available in the density range from approximately 2 to 10 lb/ft^3.

The initial weights of CO_2 gas (Q_∞, mg) in all foams were calculated using the perfect gas law and 1 atm of pressure.

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*All foams and the bonding agent were supplied by Emerson and Cuming, Inc.
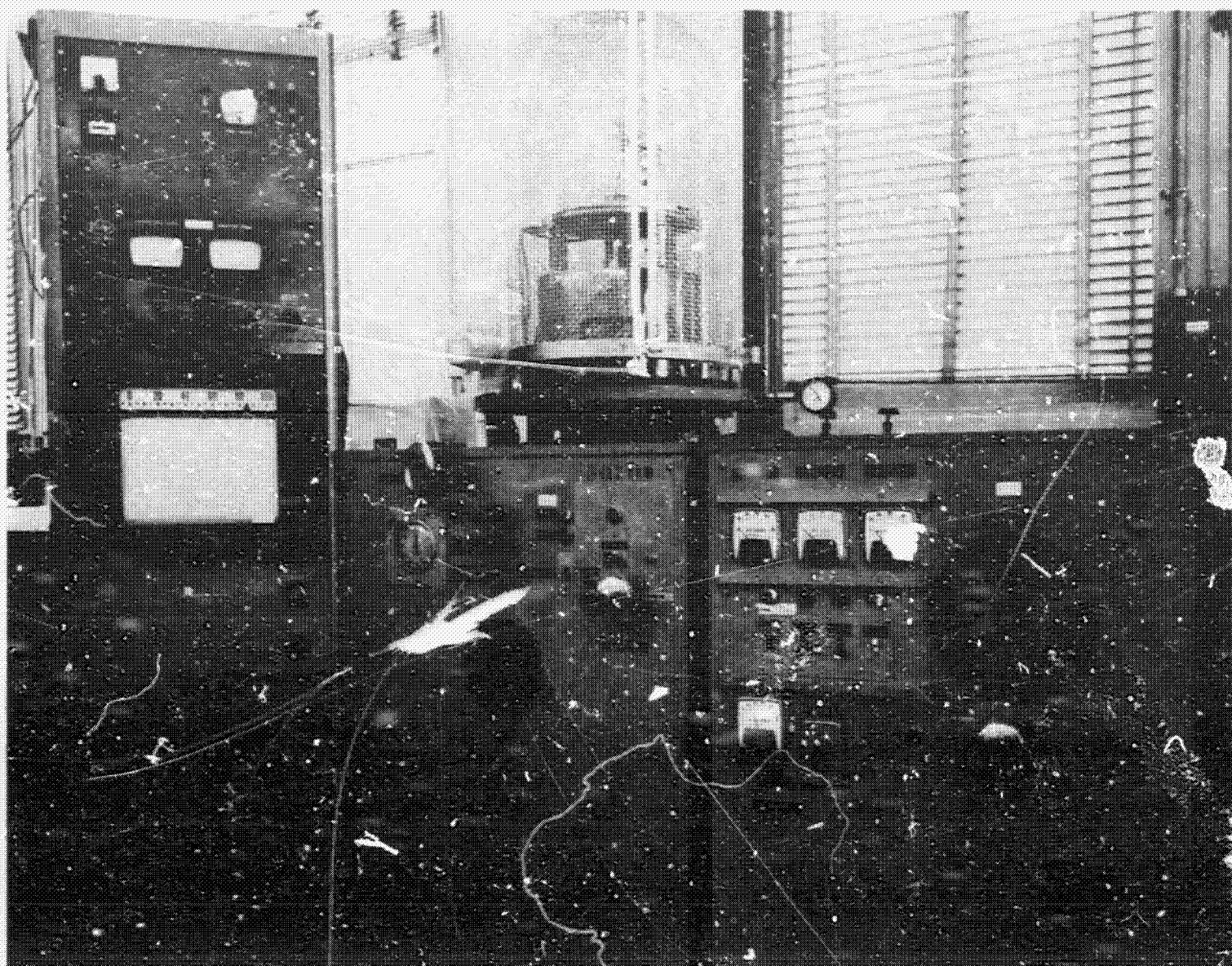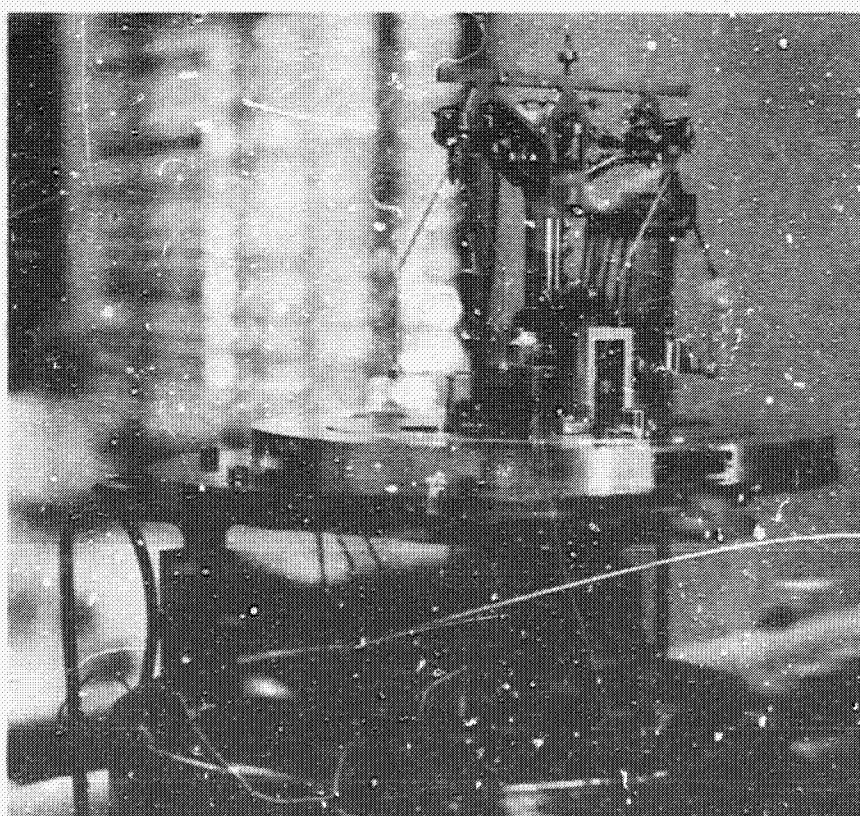
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Fig. 1. Ainsworth vacuum balance

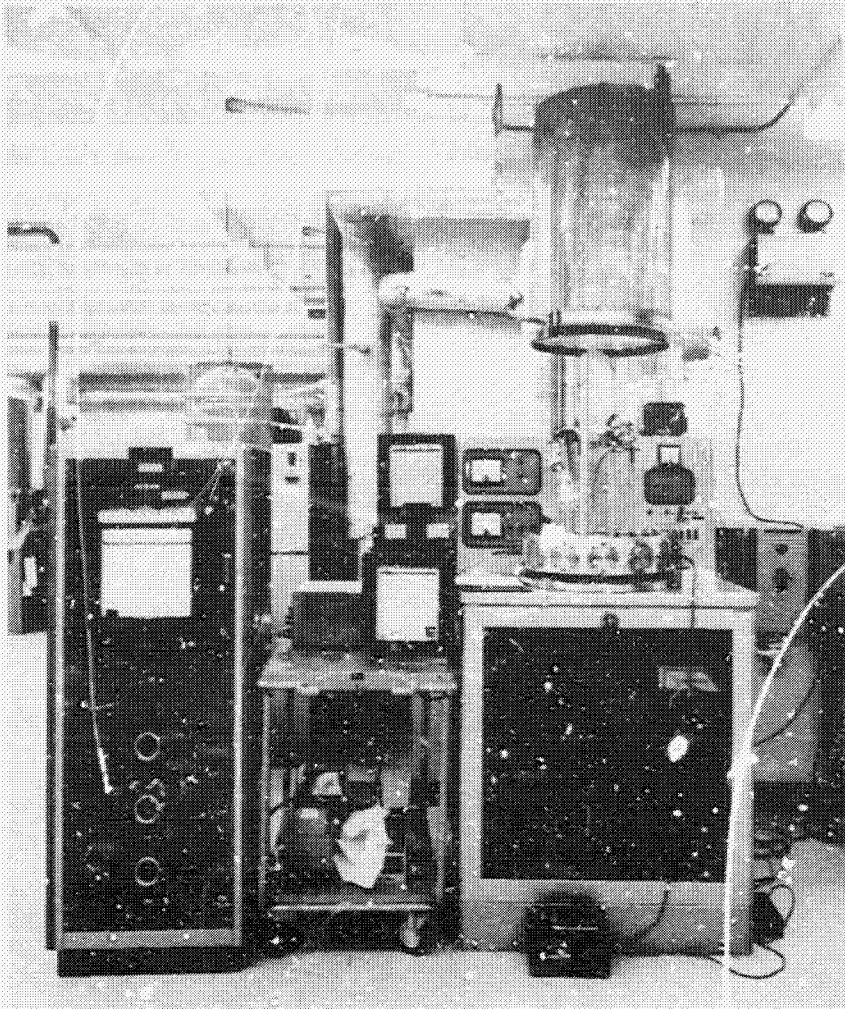**Fig. 2. Details of balance and sample suspension**

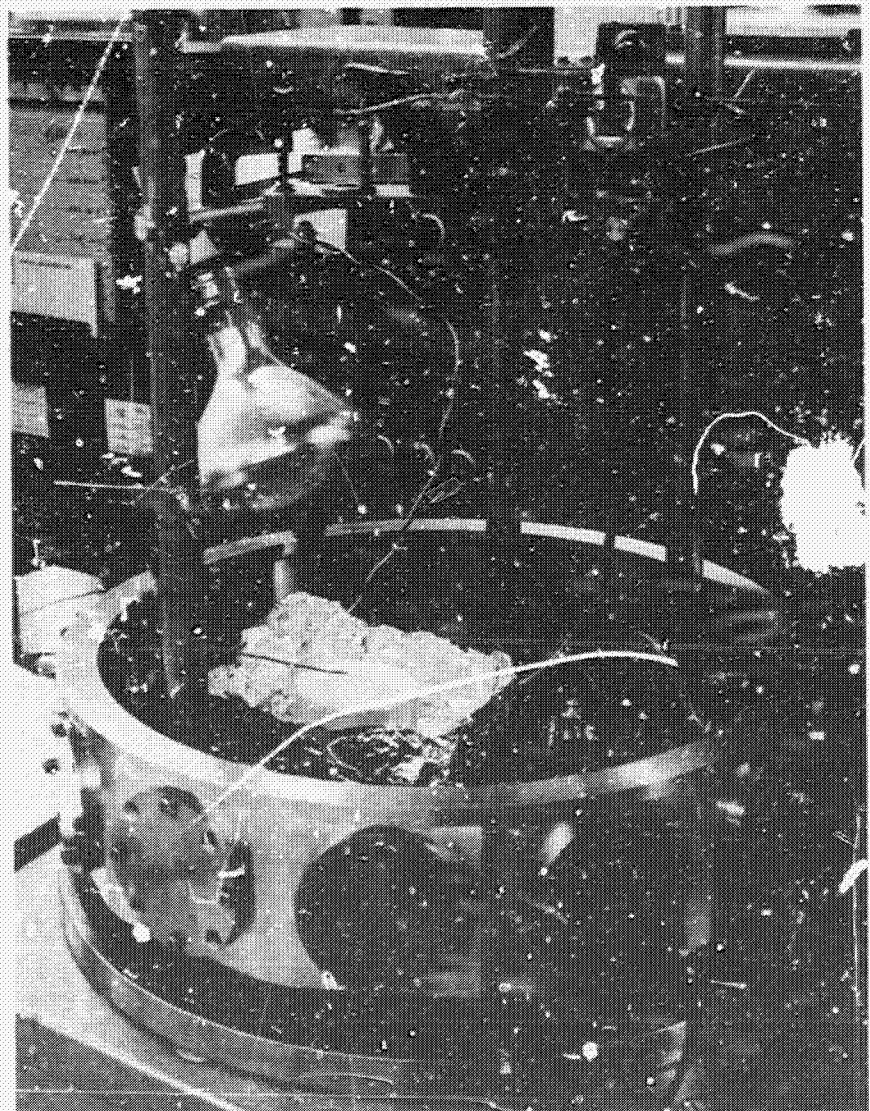Fig. 3. Vacuum-balance facility for elevated
temperature operations

Fig. 4. Details of heating and balance assembly for
elevated temperature operations

IV. RESULTS AND DISCUSSION

Weight-loss curves for Eccosil 5000, Eccofoam SH, and Stycast 1090 are shown in Fig. 5. The outgassing rates of these materials parallel the relative order of their respective gas-permeability constants (Ref. 2). Eccosil 5000 lost 130 mg of weight in 225 hr, approximately 90 mg more than the calculated CO_2 content of 90 to 100 mg (Q_∞). The additional weight loss presumably results from volatile impurities or volatile components that were not consumed in the curing reaction.

The rate of weight loss for Stycast 1090 is extremely low, as only 3.5 mg out of a possible 70 mg of gas were removed under vacuum in approximately 130 hr. This is to be expected because the CO_2 gas is contained inside glass spheres of low permeability. In addition, the high density of this material results in the formation of very thick membranes between the glass spheres.

For the Eccofoam SH, the plot of log $(Q_\infty - Q)$ vs time shown in Fig. 6 was constructed from the weight loss data (Fig. 5) and $Q_\infty = 184$ mg. Using Eq. (13) and the slope of the linear portion of the curve ($t > 120$ hr), a diffusion coefficient of 2.40×10^{-6} cm²/sec at 22°C was calculated.

Weight loss curves at 22°C for three Eccofoam FPH systems of densities 2.1, 4.5, and 6.4 lb/ft³ are shown in

Fig. 7. Using these data, plots of log $(Q_\infty - Q)$ vs time were obtained (Fig. 8), and the diffusion coefficients were found to be 6.2×10^{-7} cm²/sec for the 2.1-lb/ft³ foam, 1.76×10^{-6} cm²/sec for the 4.5-lb/ft³ foam, and
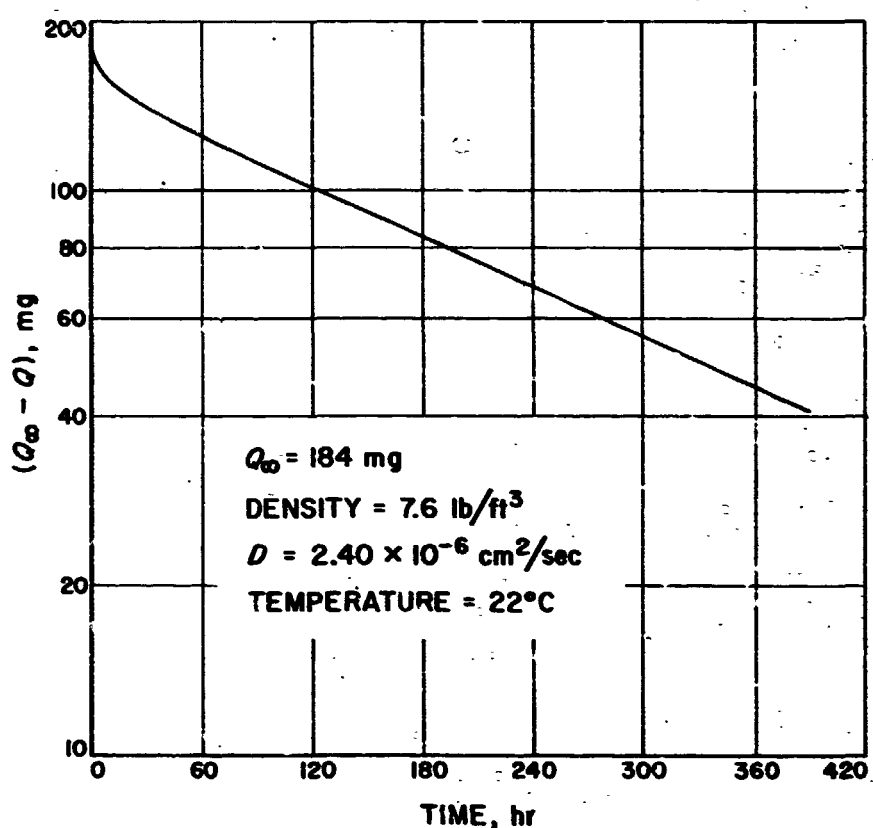

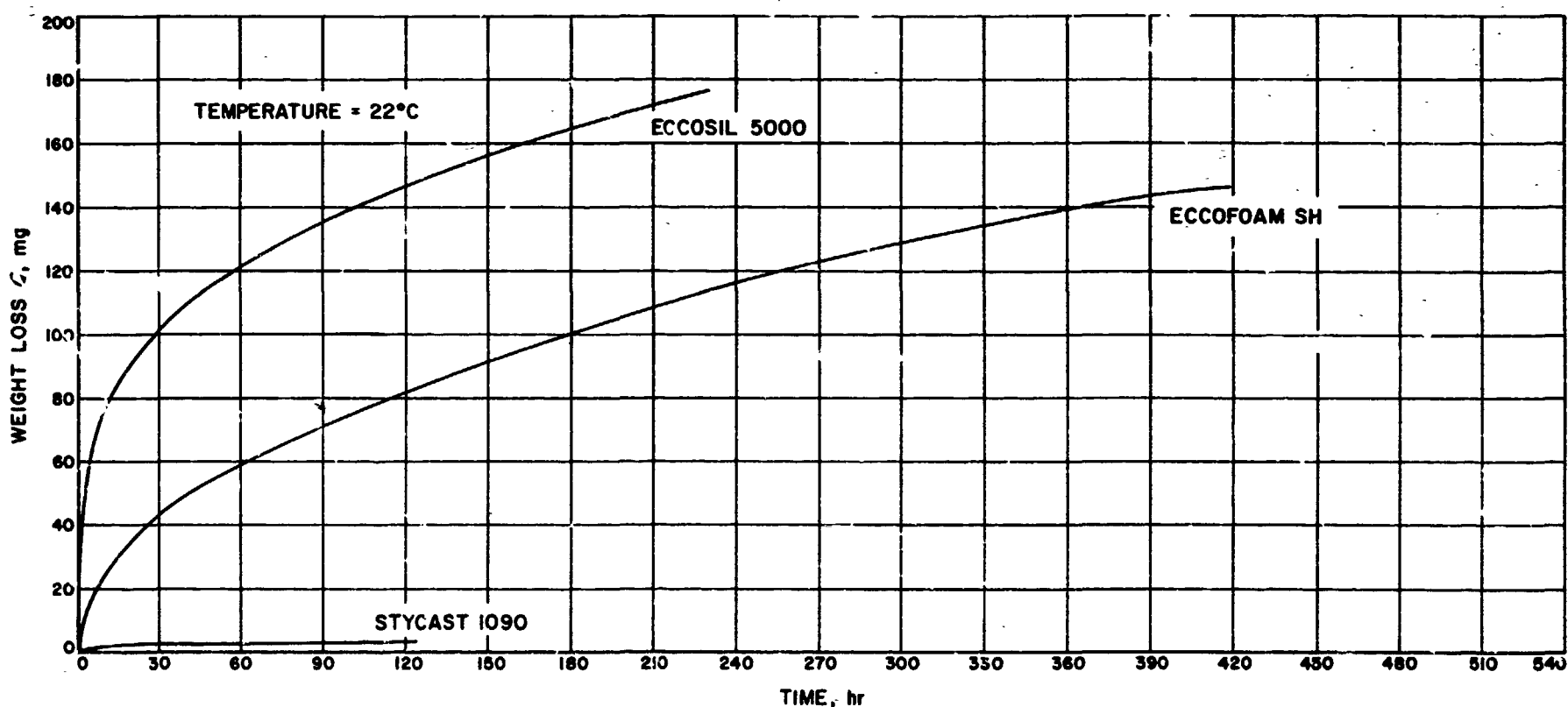**Fig. 6. Log $(Q_\infty - Q)$ vs time for Eccofoam SH at 22°C**

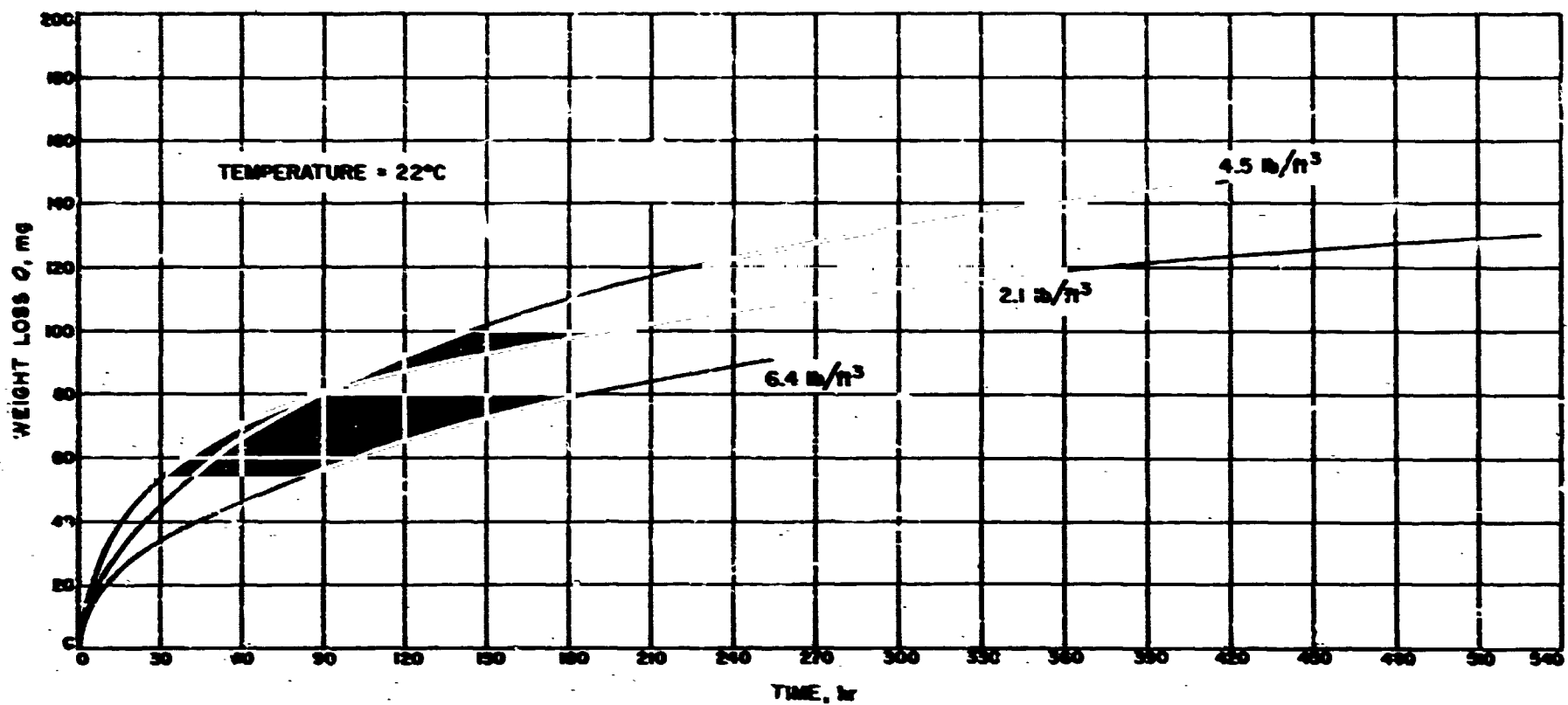

Fig. 5. Weight-loss curves for three polymer foams at 22°C

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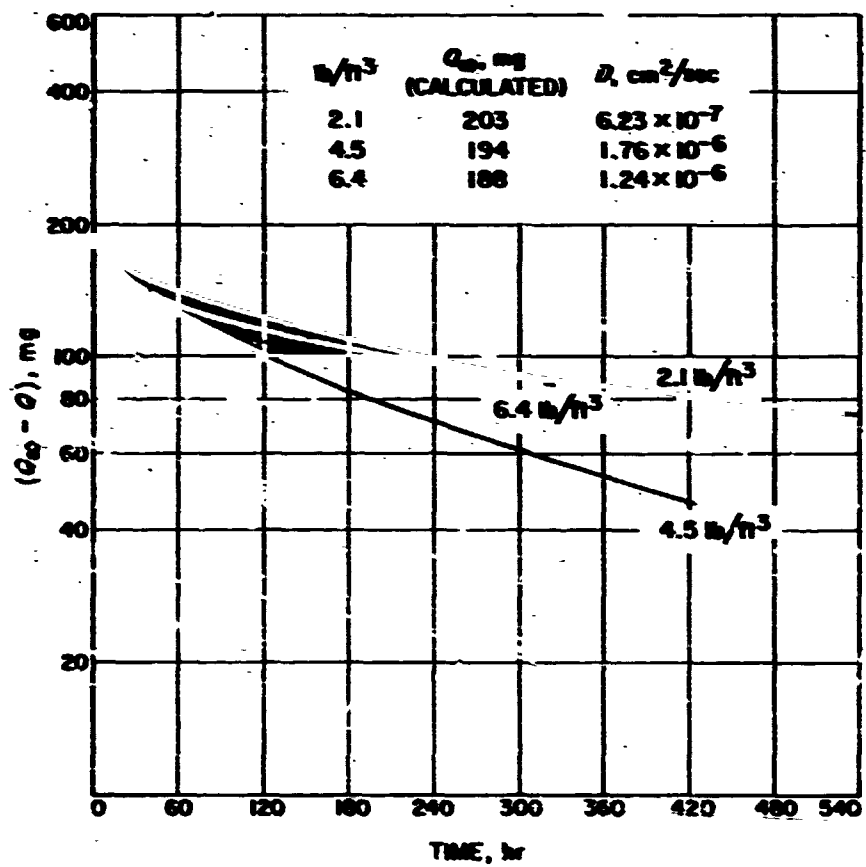Fig. 7. Weight-loss curves for Eccofoam FPH foams at 22°C

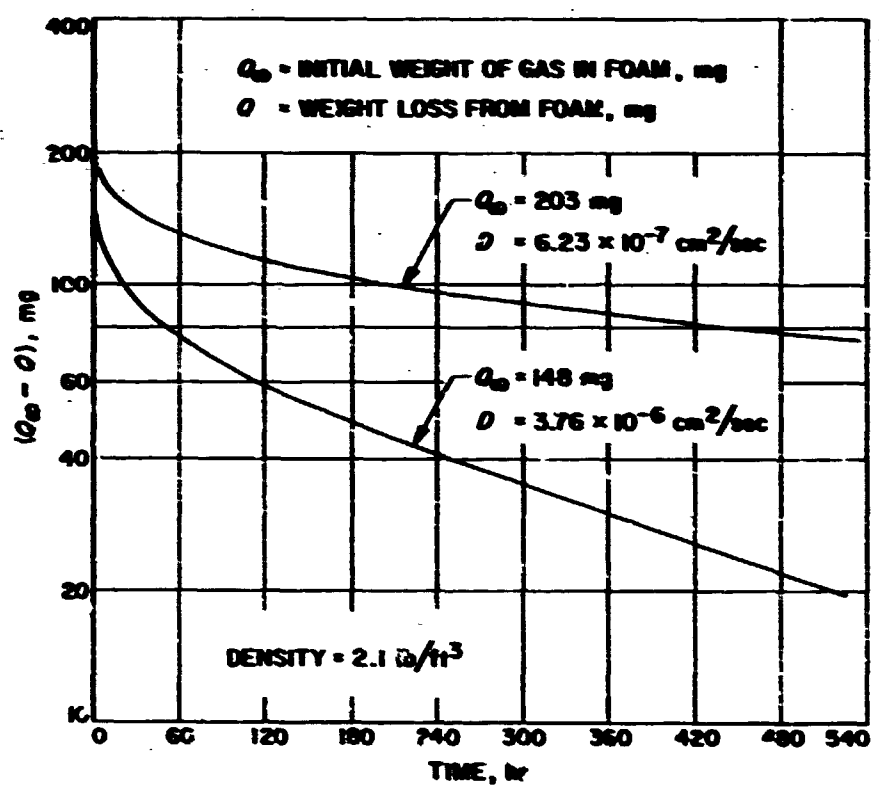Fig. 8. Log ($Q_\infty - Q$) vs time for Eccofoam FPH foams at 22°C

Fig. 9. Log ($Q_\infty - Q$) vs time for Eccofoam FPH/12/2H at 22°C

1.24×10^{-6} cm²/sec for the 6.4-lb/ft³ foam. The values used for Q_∞, which were calculated with an assumed initial gas pressure of 1 atm, were, respectively, 203 mg, 194 mg, and 188 mg of CO_2.

From Eq. (11), the diffusion coefficient should be inversely proportional to the density. This relationship holds true for the 4.5- and 6.4-lb/ft³ foams, but not for the 2.1-lb/ft³ foam, which in fact has the lowest diffusion coefficient of the three. However, this is inconsistent with the faster initial outgassing rate observed for the 2.1-lb/ft³ foam. This discrepancy can arise from an incorrectly chosen value of Q_∞. Equation (13) shows that D is inversely proportional to Q_∞. Thus a higher value of D can be obtained from the log $(Q_\infty - Q)$ plots by using a lower value of Q_∞. Support for the use of a lower value of Q_∞ can be seen from Fig. 7, where the weight loss curve for the 2.1-lb/ft³ foam is apparently approaching an asymptotic value of Q_∞ that is considerably less than the calculated value of Q_∞. From Eq. (12) and the diffusion coefficients for the 4.5- and 6.4-lb/ft³ foam, a value of 3.76×10^{-6} cm²/sec is predicted for the 2.1-lb/ft³ foam. Using the latter value for the diffusion coefficient, and the weight loss data (Fig. 5), a trial-and-error procedure

yielded a value for Q_∞ of 148 mg. Figure 9 is a plot comparing the log $(Q_\infty - Q)$ plots for Q_∞ values of 203 and 148 mg. Figure 10 is a normalized plot of Q/Q_∞ vs time for all three Eccofoam FPH foams, and it can now be seen that the weight loss curve for the 2.1-lb/ft³ foam has assumed its expected relationship in relation to the other two foams.

It should be pointed out that extrapolation to zero time of the linear portion of plots of log $(Q_\infty - Q)$ vs time should intercept at a value of log $(8Q_\infty/\pi^2)$ (Eq. 13). Thus, if the diffusion coefficient is independent of concentration, the diffusion equations will predict the value of both Q_∞ and D for a given set of weight loss vs time data. It was found that for the 6.4-lb/ft³ foam the calculated value of Q_∞ coincided with that obtained by back-extrapolation, justifying the use of the perfect gas law to calculate Q_∞.

However, extrapolation of the log $(Q_\infty - Q)$ plot for the 4.5-lb/ft³ foam did not yield the calculated value of $Q_\infty = 194$ mg. Inspection of the log $(Q_\infty - Q)$ plot for this foam shows that there is a greater drop in the initial
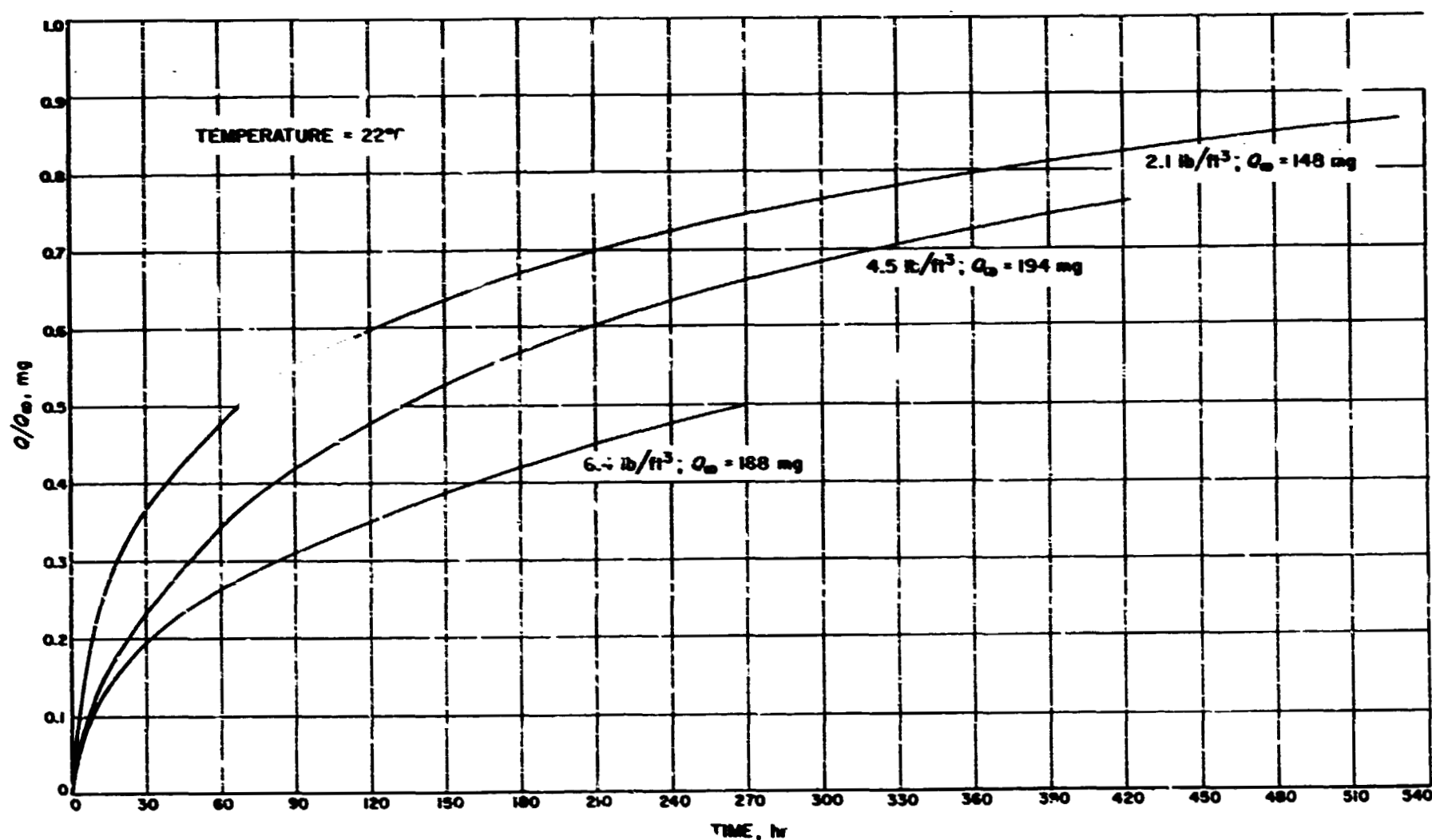

Fig. 10. Q/Q_∞ vs time for Eccofoam FPH foams at 22°C

portion of the curve than that observed for the 6.4-lb/ft³ foam. For the 2.1-lb/ft³ foam, which also failed to satisfy the equations, the drop in the initial portion of the log $(Q_\infty - Q)$ curve is greater yet. This behavior is most readily attributed to a pressure dependence of the diffusion coefficient, which becomes more pronounced with decreasing foam density. If for a polymer foam the initial diffusion coefficients are higher, then the initial portion of the log $(Q_\infty - Q)$ would drop more rapidly and then after a long time, the asymptotic diffusion coefficient can be obtained from the linear portion. But because of the initial larger drop, back-extrapolation will yield a lower value of log $(8Q_\infty/\pi^2)$, and this is observed for the 4.5- and 2.1-lb/ft³ foams.

The foregoing has shown that the initial gas contents of polymer foams of densities greater than 4.5 lb/ft³ can be determined from the perfect gas law. Also, there seems to be little if any dependence of the diffusion coefficient on pressure for densities greater than 6.4 lb/ft³ and thus both weight loss and pressure distributions can be predicted employing a single diffusion

equation and the diffusion equations for a homogeneous solid.

Using the diffusion coefficients for the 4.5- and 6.4-lb/ft³ foams, it was possible to calculate the value of the constant K in Eq. (12). This equation for the Eccofoam FPH polyurethane foams is

$$D = \frac{7.9 \times 10^{-6}}{\rho}$$

where D is in units of cm²/sec and ρ in units of lb/ft³.

The permeation constant of the bulk polyurethane polymer comprising the foam material can now be calculated from Eq. (11), using the experimentally obtained diffusion coefficients. This procedure yielded a value of P_e equal to 5.1×10^{-9} (cc STP) mm/sec/cm²/cm Hg, which can be compared to a value of 12×10^{-9} reported for rubbery polyurethanes (Ref. 2). However, a lower P_e value for the rigid foam material would be expected in comparison to the equivalent rubbery material (Ref. 2).

V. TEMPERATURE DEPENDENCE

Outgassing rates for a 4.5-lb/ft³ foam were determined at 22, 41, 61, and 81°C. The tests were conducted by first heating the samples in air to the desired temperature and then subjecting them to a vacuum. It was found, however, that the samples heated in air would lose an amount of CO_2 which increased with increasing temperature. It became a practice therefore to start recording the weight loss in air during heating. When the desired
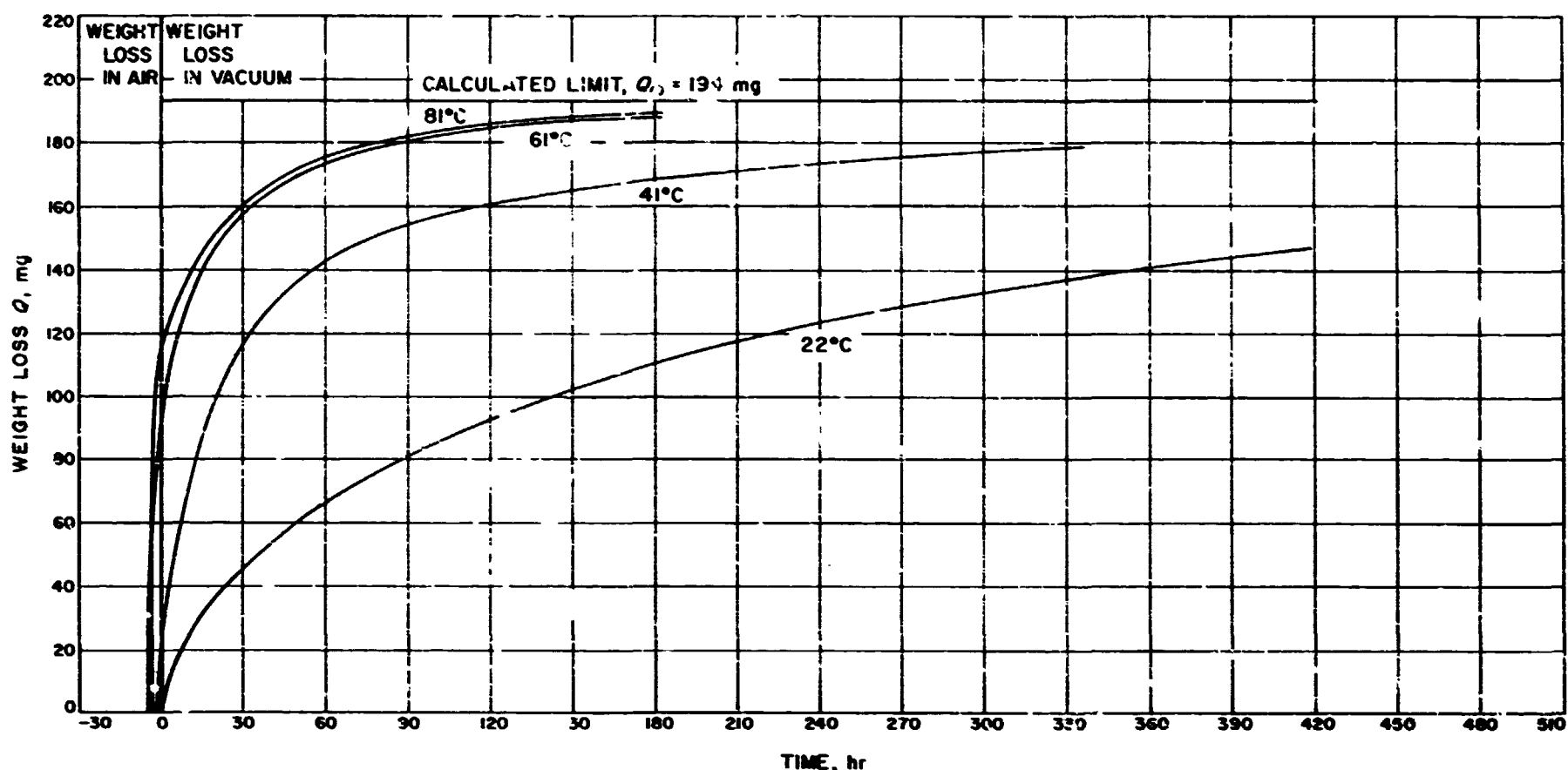
Fig. 11. Temperature dependence of the outgassing rate for an Eccofoam FPH/12/6H foam of density 4.5 lb/ft³

temperature was reached and the weight loss rate slowed significantly, vacuum was applied. The results of the tests are given in Fig. 11, which shows weight loss both in air and in vacuum with zero time taken as the point when vacuum was initiated.

The curves in Fig. 11 show a dramatic increase in the rate of gas removal with increasing temperature. The largest change occurs between 22 and 61°C. Above 61°C the changes are small. It is instructive to observe that at the higher temperatures, the weight loss asymptote appears to be the value of $Q_\infty = 194$ mg, which was calculated from the perfect gas law. This further justifies the use of this value in determining the diffusion coefficients from plots of log $(Q_\infty - Q)$. Using the same value of $Q_\infty = 194$ mg, it is seen that this foam has lost approximately 97.5% of its gas content in 180 hr at 61°C and higher, whereas only 57% of the gas content was lost in 180 hr at 22°C.

The diffusion coefficients obtained at the various temperatures are plotted in Fig. 12 as log D vs $1/T$ in °K. The general appearance of this curve is sigmoidal and indicates that the largest changes in the diffusion coefficient occur between 22 and 81°C, above and below which there appears to be only a gradual dependence of log D on $1/T$.
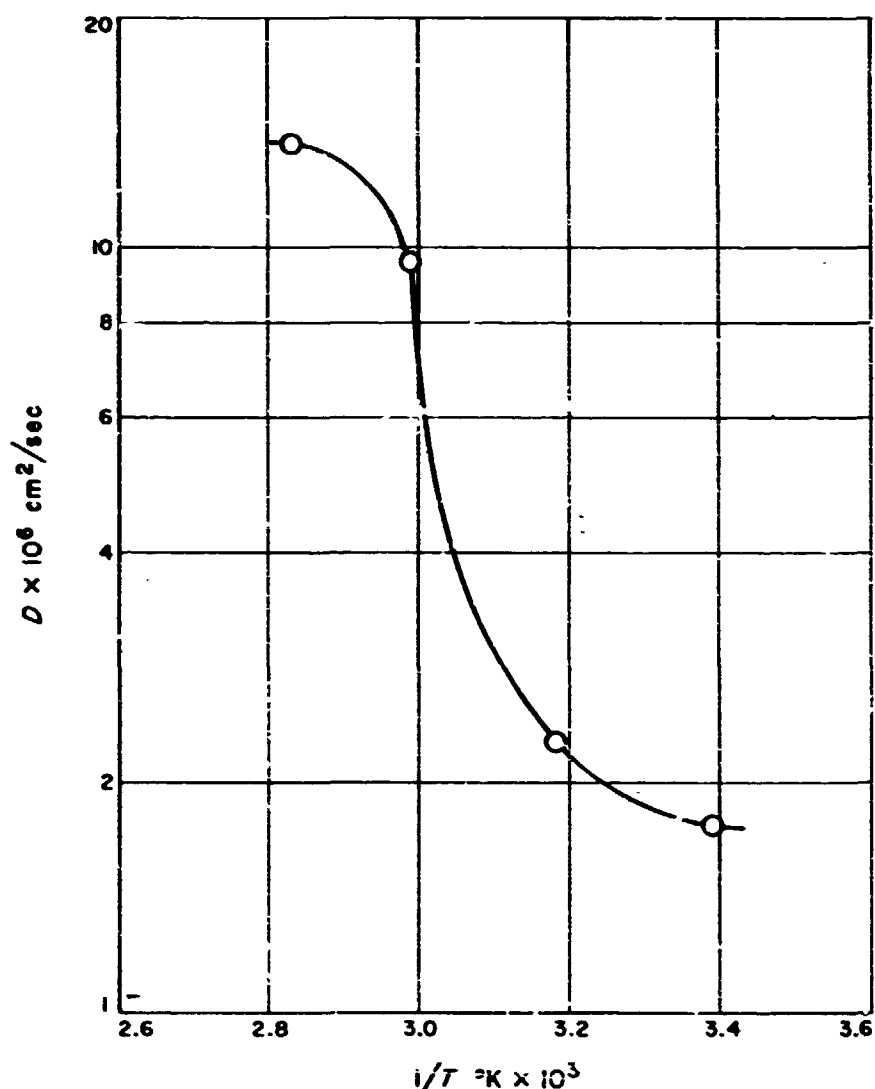

Fig. 12. Log D vs $1/T$ °K for an Eccofoam FPH/.2/6H foam of density 4.5 lb/ft³

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